

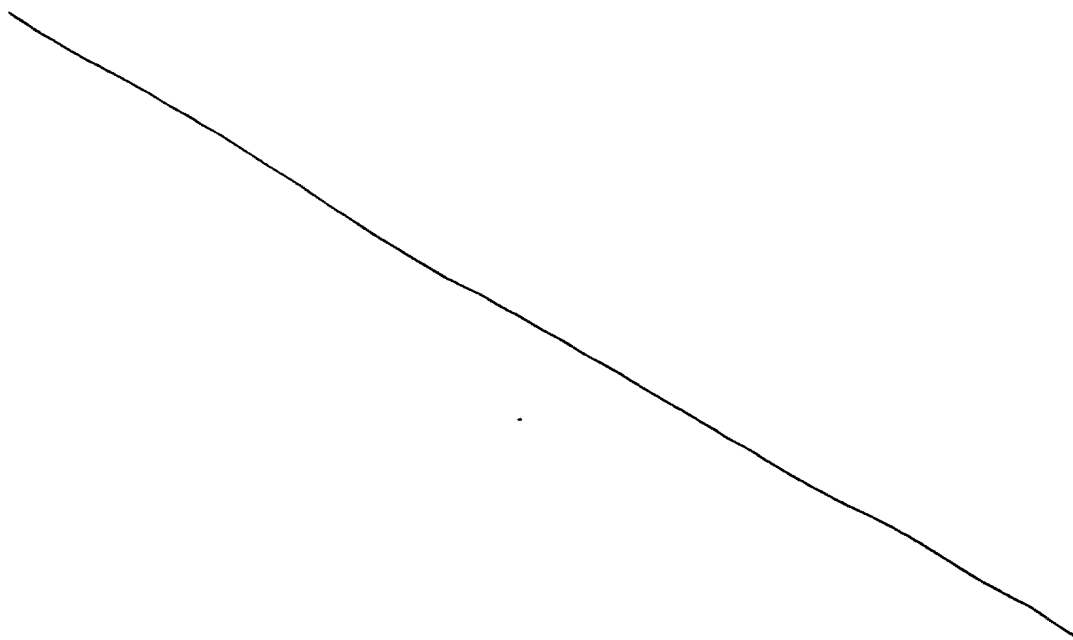
WHAT IS CLAIMED IS:

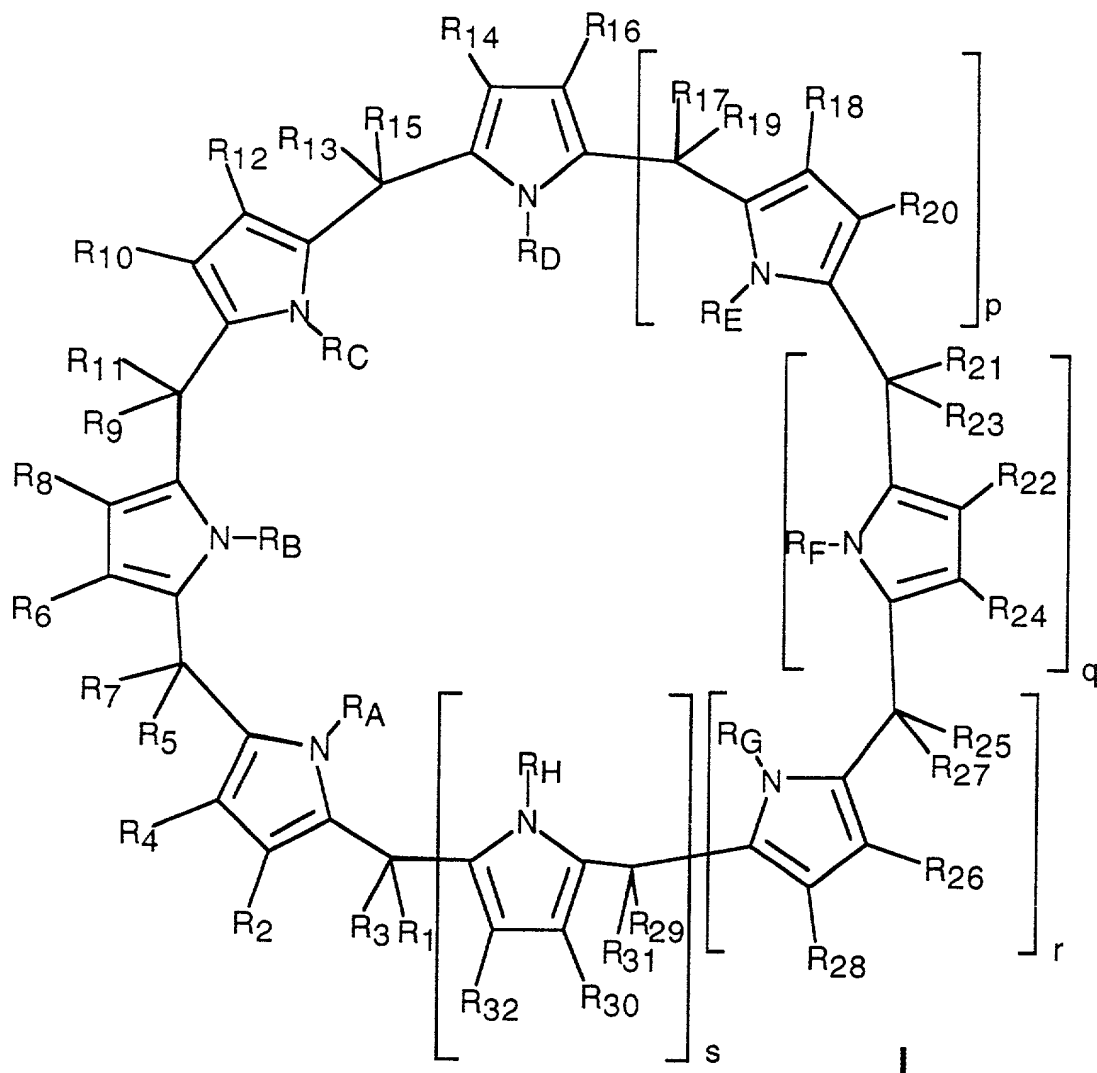
1. A calix[n]pyrrole macrocycle where n is 4, 5, 6, 7, or 8; or a calix[m]pyridino[n]pyrrole macrocycle where m + n is 4, 5, 6, 7, or 8 and m and n are other than zero; the macrocycle
5 noncovalently-complexed to a molecular or anionic species.

2. A calix[n]pyrrole macrocycle where n is 4, 5, 6, 7, or 8; a calix[m]pyridino[n]pyrrole macrocycle where m + n is 4, 5, 6, 7, or 8 and m and n are other than zero; or a calix[m]pyridine where m is 4, 5, 6, 7, or 8; where the macrocycle attached to a solid support.
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3. A calix[n]pyrrole macrocycle where n is 4, 5, 6, 7, or 8; calix[m]pyridino[n]pyrrole macrocycle where m + n is 4, 5, 6, 7, or 8, and m and n are other than zero; or calix[m]pyridine macrocycle where m is 4, 5, 6, 7, or 8 having a first conformation in a solid state when unbound to a molecular or anionic species and having a second conformation in a solid state when bound to a molecular or anionic species.
15

4. The macrocycle of claim 1, 2, or 3 wherein the macrocycle is a calix[n]pyrrole and the calix[n]pyrrole has structure I:





wherein

when n is 4, $p = q = r = s = 0$, $R_1 - R_{16}$ are independently substituents as listed in paragraph i) below, and $R_A - R_D$ are independently substituents as listed in paragraph ii) below;

when n is 5, $p = 1$, $q = r = s = 0$, R_1 to R_{20} are independently substituents as listed in paragraph i) below, and $R_A - R_E$ are independently substituents as listed in paragraph ii) below;

when n is 6, $p = q = 1$, $r = s = 0$, R_1 to R_{24} are independently substituents as listed in paragraph i) below, and $R_A - R_F$ are independently substituents as listed in paragraph ii) below;

when n is 7, $p = q = r = 1$, $s = 0$, R_1 to R_{28} are independently substituents as listed in paragraph i) below, and $R_A - R_G$ are independently substituents as listed in paragraph ii) below;

when n is 8, $p = q = r = s = 1$, R_1 to R_{32} are independently substituents as listed in paragraph i) below, and $R_A - R_H$ are independently substituents as listed in paragraph ii) below;

i) hydrogen, halide, hydroxyl, alkyl, alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl, hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl, hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxyamide, carboxyamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, tetrahydropyran, tetrahydrothiapyran, thioalkyl, haloalkyl, haloalkenyl, haloalkynyl, alkyl ester, a site-directing molecule, a catalytic group, a reporter group, a binding agent, or a couple that is coupled to a site-directing molecule, to a catalytic group, to a reporter group, or to a binding agent;

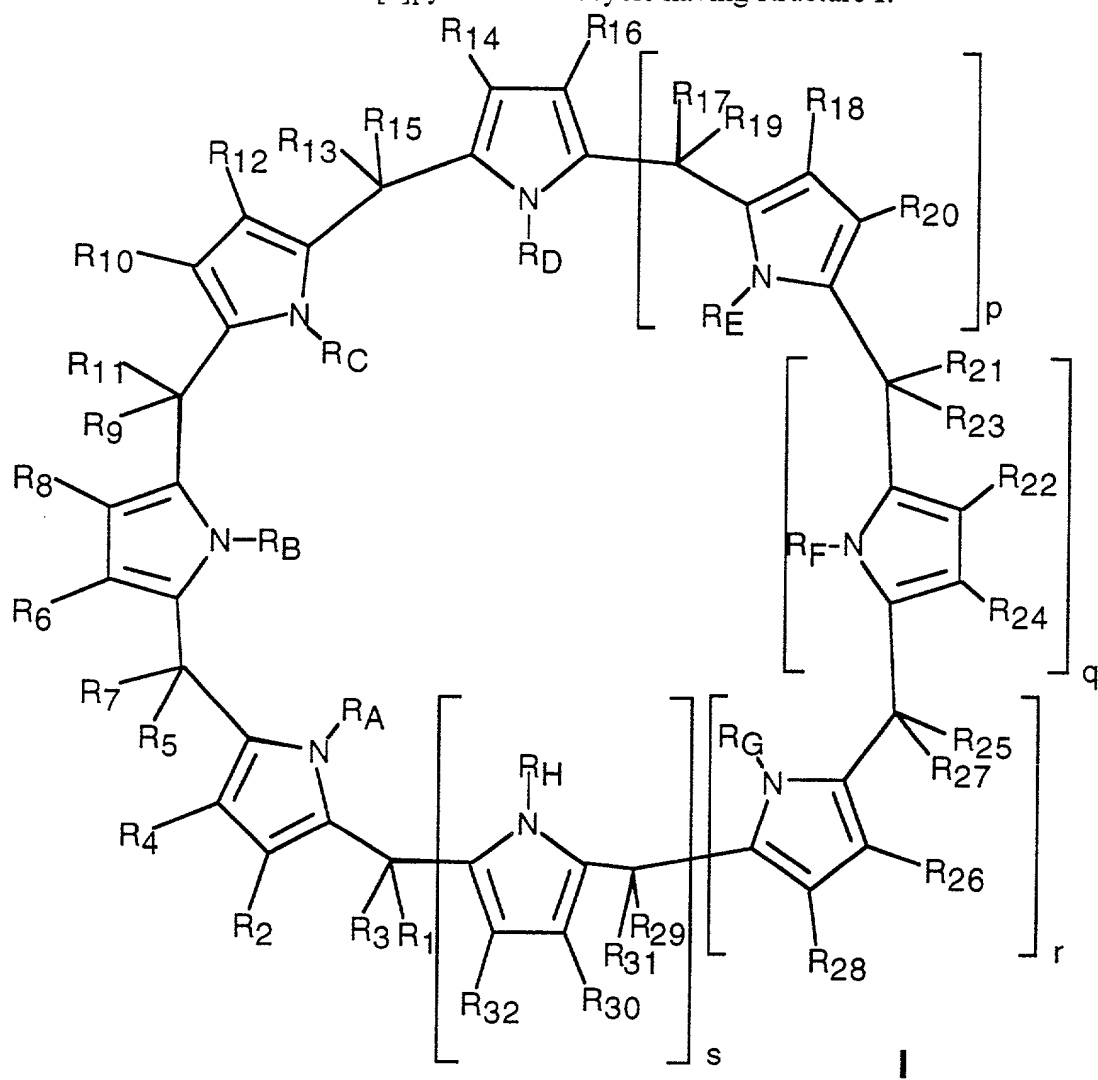
ii) hydrogen, alkyl, aminoalkyl, alkylsulfone, carboxy alkyl, carboxyamidealkyl, phospho alkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, haloalkyl, aryl, N-oxide, dialkylamino, carbamate, or arylsulfonyl;

or

at least two substituents are coupled to form a bridged structure, and when coupled to form a bridged structure, nonbridged substituents are as defined herein in paragraph i) or ii);

wherein odd-numbered R-substituents are other than hydrogen.

5. A β -substituted calix[n]pyrrole macrocycle having structure I:



wherein

n is 4, 5, 6, 7 or 8;

when n is 4, $p = q = r = s = 0$, $R_1 - R_{16}$ are independently substituents as listed in paragraph i) below, and $R_A - R_D$ are independently substituents as listed in paragraph ii) below;

when n is 5, $p = 1$, $q = r = s = 0$, R_1 to R_{20} are independently substituents as listed in paragraph i) below, and $R_A - R_E$ are independently substituents as listed in paragraph ii) below;

when n is 6, $p = q = 1$, $r = s = 0$, R_1 to R_{24} are independently substituents as listed in paragraph i) below, and $R_A - R_F$ are independently substituents as listed in paragraph ii) below;

when n is 7, $p = q = r = 1$, $s = 0$, R_1 to R_{28} are independently substituents as listed in paragraph i) below, and $R_A - R_G$ are independently substituents as listed in paragraph ii) below;

when n is 8, $p = q = r = s = 1$, R_1 to R_{32} are independently substituents as listed in paragraph i) below, and $R_A - R_H$ are independently substituents as listed in paragraph ii) below;

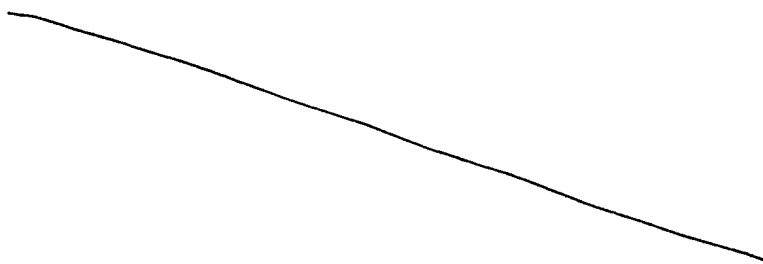
i) hydrogen, halide, hydroxyl, alkyl, alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl, hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl, hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxamide, carboxamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, tetrahydropyran, tetrahydrothiapyran, thioalkyl, haloalkyl, haloalkenyl, haloalkynyl, alkyl ester, a site-directing molecule, a catalytic group, a reporter group, a binding agent, or a couple that is coupled to a site-directing molecule, to a catalytic group, to a reporter group, or to a binding agent;

ii) hydrogen, alkyl, aminoalkyl, alkylsulfone, carboxy alkyl, carboxamidealkyl, phospho alkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, halo alkyl, aryl, N-oxide, dialkylamino, carbamate, or arylsulfonyl;

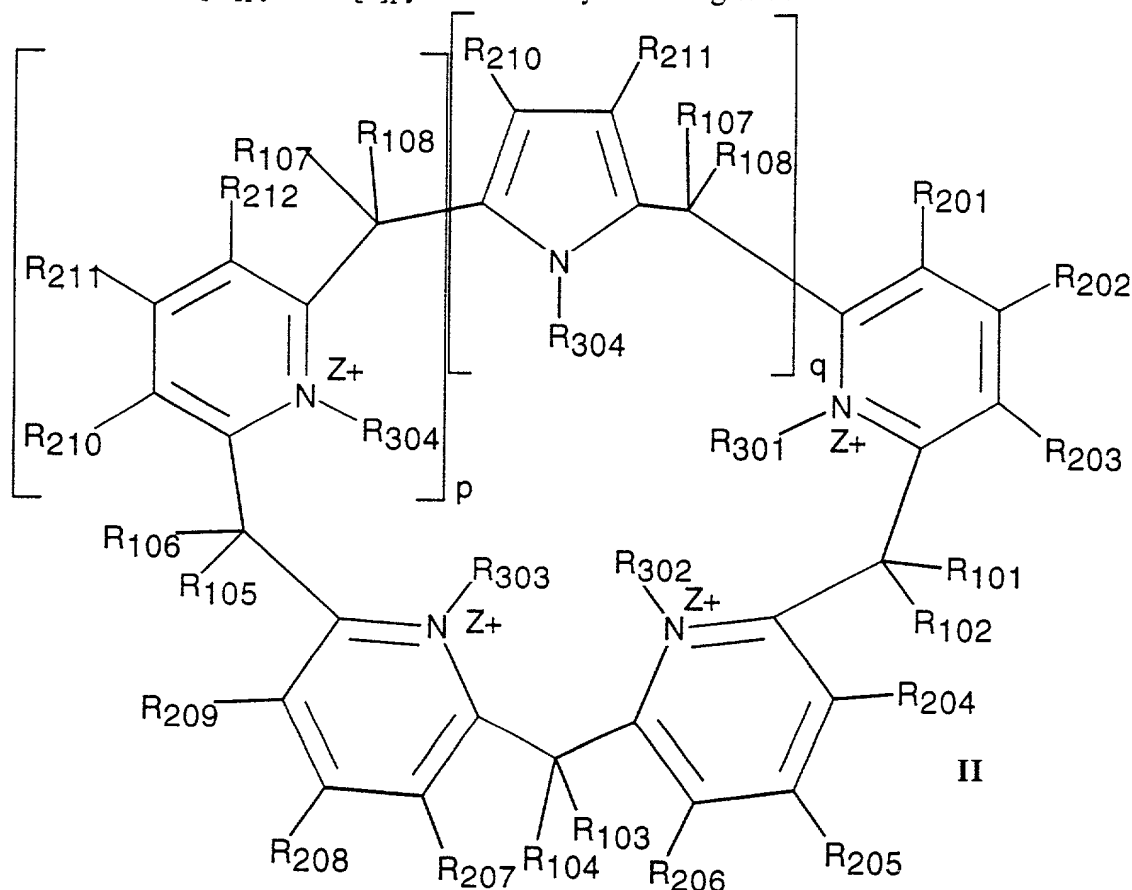
or

at least two substituents may be coupled to form a bridged structure, and when coupled to form a bridged structure, nonbridged substituents are as defined herein in paragraph i) or ii); and

wherein at least one even-numbered R-substituent and all odd-numbered R-substituents are other than hydrogen.



6. A calix[m]pyridino[n]pyrrole macrocycle having structure II:



wherein m designates a number of pyridines in the macrocycle and n designates a number of pyrroles in the macrocycle;

$m+n=4$;

m is other than 1 or 2;

when m is 4, n = 0, p = 1, q = 0, R101 to R108 and R201 to R212 are independently substituents as listed in paragraph i) below, and R301 - R304 are independently substituents as listed in paragraph ii) below;

when m is 3, n = 1, p = 0, q = 1, R101 to R108 and R201 to R211 are independently substituents as listed in paragraph i) below, and R301 - R304 are independently substituents as listed in paragraph ii) below;

i) hydrogen, halide, hydroxyl, alkyl, alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl, hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl, hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxamide, carboxamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide,

5 tetrahydropyran, tetrahydrothiapyran, thioalkyl, haloalkyl, haloalkenyl, haloalkynyl, alkyl ester, a site-directing molecule, a catalytic group, a reporter group, a binding agent, or a couple that is coupled to a site-directing molecule, to a catalytic group, to a reporter group, or to a binding agent;

10 ii) a lone pair of electrons, hydrogen, alkyl, aminoalkyl, alkylsulfone, carboxy alkyl, carboxyamidealkyl, phospho alkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, halo alkyl, aryl, N-oxide, dialkylamino, carbamate, or arylsulfonyl;

or

at least two substituents are coupled to form a bridged structure, and when coupled to form a bridged structure, nonbridged substituents are as defined herein in paragraph i) or ii);

15 wherein R_{101} - R_{108} are other than hydrogen;

wherein when R_{301} - R_{304} is other than a lone pair of electrons, Z is 1;

20 wherein when R_{301} - R_{304} is a lone pair of electrons, Z is 0.

7. A calix[m]pyridino[n]pyrrole macrocycle

where

25 m and n designate a number of pyridines and pyrroles in the macrocycle, respectively, m and n are other than 0, and $m+n=5, 6, 7, \text{ or } 8$;

each pyridine or pyrrole α -carbon is bound to another pyridine or pyrrole α -carbon *via* one non hydrogen-linked sp^3 hybridized *meso*-carbon;

30 each sp^3 hybridized *meso*-carbon is further independently bonded to a halide, hydroxyl, alkyl, alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl, hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl, hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxyamide, carboxyamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, tetrahydropyran, thioalkyl, haloalkyl, haloalkenyl, haloalkynyl or alkyl ester group; to a site-directing molecule; to a

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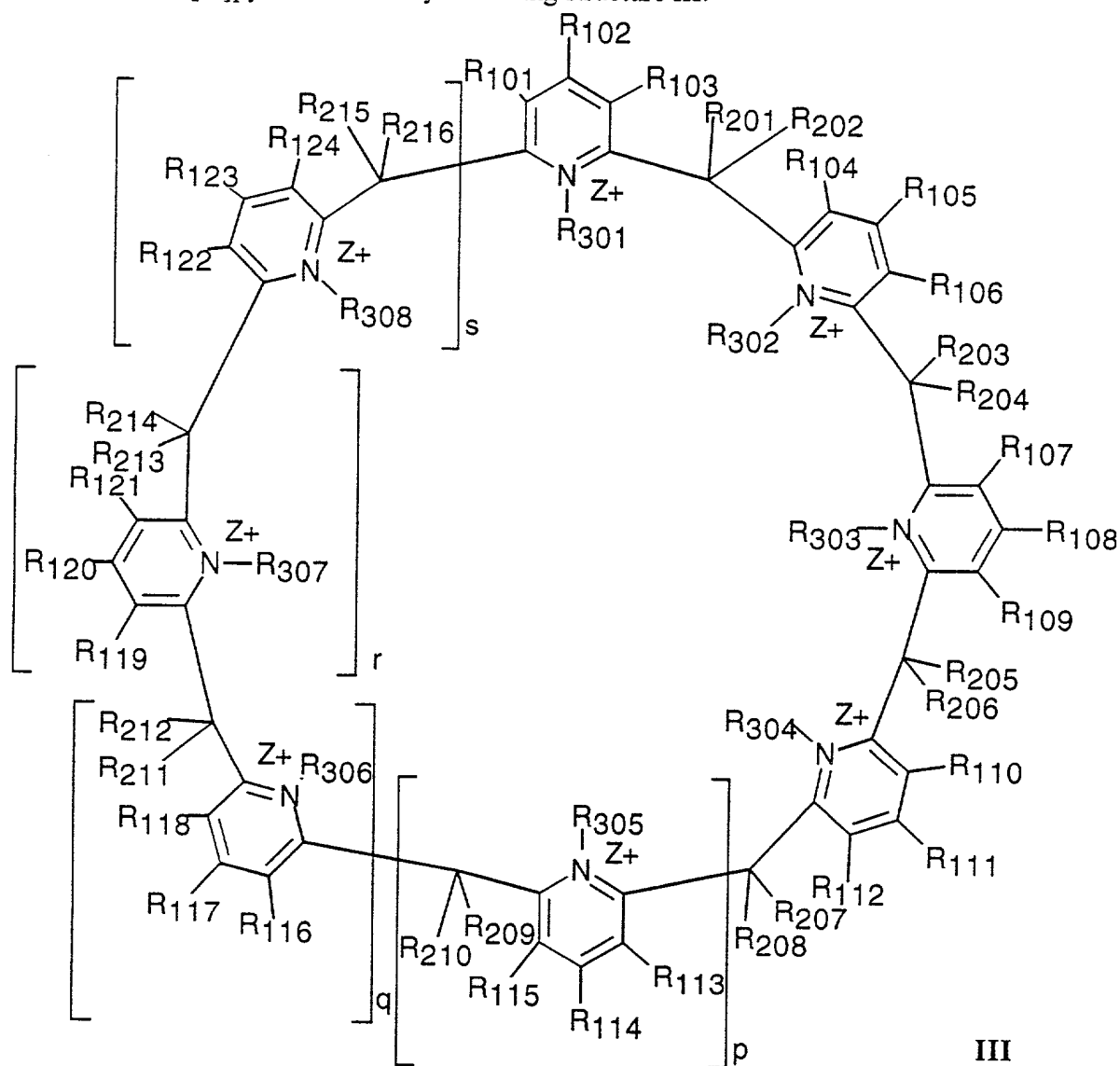
5 catalytic group; to a reporter group; to a binding agent; or to a couple that is coupled to a site-directing molecule, to a catalytic group, to a reporter group, or to a binding agent;
each pyridine β carbon, pyrrole β carbon and pyridine γ carbon is
independently bonded to a hydrogen, halide, hydroxyl, alkyl,
alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl,
hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl,
hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxamide,
carboxamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl
sulfoxide, alkyl sulfone, alkyl sulfide, tetrahydropyran, thioalkyl,
haloalkyl, haloalkenyl, haloalkynyl, alkyl ester group; to a site-
directing molecule; to a catalytic group; to a reporter group; to a
binding agent; or to a couple that is coupled to a site-directing
molecule; to a catalytic group; to a reporter group, or to a binding
agent;

each pyridine or pyrrole nitrogen is bound to a lone pair of electrons,
hydrogen, alkyl, aminoalkyl, alkylsulfone, carboxy alkyl,
carboxamidealkyl, phospho alkyl, alkyl sulfoxide, alkyl sulfone,
alkyl sulfide, halo alkyl, aryl, N-oxide, dialkylamino, carbamate, or
arylsulfonyl; and

or

at least one sp^3 hybridized *meso*-carbon, pyridine β -carbon, pyrrole β -
carbon, pyridine γ carbon, pyrrole nitrogen or pyridine nitrogen is
coupled to form a bridged structure to itself or to another sp^3
hybridized *meso*-carbon, pyridine β -carbon, pyrrole β -carbon,
pyridine γ carbon, pyrrole nitrogen, or pyridine nitrogen; and when
coupled to form a bridged structure, non-bridged atoms are as
defined for an sp^3 hybridized *meso*-carbon, pyridine β -carbon,
pyrrole β -carbon, pyridine γ carbon, pyrrole nitrogen, or pyridine
nitrogen.

8. A calix[m]pyridine macrocycle having structure III:



wherein m is 4, 5, 6, 7 or 8;

when m is 4, $p = q = r = s = 0$, R101 to R112 and R201 to R208 are independently substituents as listed in paragraph i) below, and R301 - R304 are independently substituents as listed in paragraph ii) below;

when m is 5, $p = 1$, $q = r = s = 0$, R101 to R115 and R201 to R210 are independently substituents as listed in paragraph i) below, and R301 - R305 are independently substituents as listed in paragraph ii) below;

when m is 6, $p = q = 1$, $r = s = 0$, R101 to R118 and R201 to R212 are independently substituents as listed in paragraph i) below, and R301 - R306 are independently substituents as listed in paragraph ii) below;

when m is 7, $p = q = r = 1$, $s = 0$, R₁₀₁ to R₁₂₁ and R₂₀₁ to R₂₁₄ are independently substituents as listed in paragraph i) below, and R₃₀₁ - R₃₀₇ are independently substituents as listed in paragraph ii) below;

when m is 8, $p = q = r = s = 1$, R₁₀₁ to R₁₂₄ and R₂₀₁ to R₂₁₆ are independently substituents as listed in paragraph i) below, and R₃₀₁ - R₃₀₈ are independently substituents as listed in paragraph ii) below;

i) hydrogen, halide, hydroxyl, alkyl, alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl, hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl, hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxamide, carboxamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, tetrahydrotetrapyrane, thioalkyl, haloalkyl, haloalkenyl, haloalkynyl, alkyl ester, a site-directing molecule, a catalytic group, a reporter group, a binding agent, or a couple that is coupled to a site-directing molecule, to a catalytic group, to a reporter group, or to a binding agent;

ii) a lone pair of electrons, hydrogen, alkyl, aminoalkyl, alkylsulfone, carboxy alkyl, carboxamidealkyl, phospho alkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, halo alkyl, aryl, N-oxide, dialkylamino, carbamate, or arylsulfonyl; and

or

at least two substituents are coupled to form a bridged structure, and when coupled to form a bridged structure, nonbridged substituents are as defined herein in paragraph i) or ii) other than for bridged substituents;

wherein R₂₀₁-R₂₁₆ are other than hydrogen;

wherein when R₃₀₁-R_{30m} is other than a lone pair of electrons, Z is 1; and

wherein when R₃₀₁-R_{30m} is a lone pair of electrons, Z is 0.

9. The macrocycle of any one of claims 5-8 wherein the site-directing molecule is an oligonucleotide, an antibody, or a peptide having affinity for a biological receptor.

10. The macrocycle of any one of claims 5-8 wherein the binding agent is a calix[n]pyrrole where n is 4, 5, 6, 7, or 8, a calix[m]pyridino[n]pyrrole where m + n is 4, 5, 6, 7, or 8, and m and n are not 0, a calixarene, a cation-binding functionality, a crown ether, a chelating group, a porphyrin, or an expanded porphyrin.

11. The macrocycle of any one of claims 5-8 wherein the reporter group is a redox active group, or a fluorescent molecule.

12. The macrocycle of claim 11 wherein the redox active group is ferrocene.

13. The macrocycle of claim 5, 6, 7, or 8 wherein at least one R substituent attached to a *meso*-carbon is carboxy or carboxyalkyl.

14. The macrocycle of claim 5, 6, 7, or 8 wherein at least one R substituent attached to a non- α , non-*meso*, macrocyclic carbon.

15. The macrocycle of claim 5, 6, 7, or 8 wherein at least one R substituent attached to a non- α , non-*meso*, macrocyclic carbon is carboxy, carboxyalkyl, ester, or carboxamide.

16. The macrocycle of claim 5, 6, 7, or 8 wherein at least one macrocyclic nitrogen is bound to hydrogen.

17. The macrocycle of claim 5 where n is 4, R_A-R_D are each hydrogen, odd-numbered R groups are methyl, one even-numbered R group is (CH₂)_tCOOH where 0 ≤ t ≤ 10, and even-numbered R groups that are other than (CH₂)_tCOOH are hydrogen.

18. The macrocycle of claim 80 where n is 4, where pyrrolic nitrogens are attached to hydrogen atoms, each of three *meso*-carbons is bridged to itself in a spirocyclohexyl substituent, one *meso*-carbon is bonded to a methyl group and to -CH₂CH₂CH₂COOH, and pyrrole β-carbons are bound to hydrogen.

19. A calix[n]pyrrole where n is 5, 6, 7, or 8.

20. A chiral calix[n]pyrrole where n is 4, 5, 6, 7 or 8.

21. A method of making a calix[n]pyrrole where n is 5, 6, 7, or 8, the calix[n]pyrrole having different substituents at a *meso*-carbon atom, comprising

reacting pyrrole and at least two ketone molecules to produce a calix[n]pyrrole having different substituents at the *meso*-carbon atoms.

22. The method of claim 21 where the number of different ketone molecules includes acetone and cyclohexanone.

23. A method of making a calix[n]pyrrole where n is 4, 5, 6, 7, or 8, the calix[n]pyrrole having an ester substituent, comprising

reacting an ester-functionalized ketone, pyrrole, and a ketone, to produce a calix[n]pyrrole having an ester substituent.

24. The method of claim 23 wherein the ester-functionalized ketone is methyl-4-acetylbutyrate, and the ketone is cyclohexanone, acetone, or pentan-3-one.

25. A method of making a calix[n]pyrrole where n is 4, 5, 6, 7, or 8, the calix[n]pyrrole having an acid substituent, comprising

reacting an ester-functionalized ketone, pyrrole and a ketone to produce a calix[n]pyrrole ester derivative; and

de-esterifying the ester derivative to produce a calix[n]pyrrole monoacid derivative.

26. A method of making a β -substituted calix[n]pyrrole where n is 4, 5, 6, 7, or 8 comprising

activating a calix[n]pyrrole where n is 4, 5, 6, 7, or 8; and

reacting the activated calix[n]pyrrole with an electrophile.

27. The method of claim 26 where the activating is deprotonating the calix[n]pyrrole using a Brønsted base, or a Brønsted base in conjunction with a complexing agent.

28. The method of claim 26 where the electrophile is carbon dioxide.

29. The method of claim 26 where the electrophile is ethylbromoacetate.

30. A method of making a β -substituted calix[n]pyrrole where n is 4, 5, 6, 7, or 8 comprising

reacting a β -substituted pyrrole and a ketone to produce a β -substituted calix[n]pyrrole.

31. The method of claim 30 wherein the β -substituted pyrrole is 3,4-dimethoxypyrrole, and the ketone is cyclohexanone, acetone, or pentan-3-one.

32. A method of making a β -substituted calix[n]pyrrole where n is 4, 5, 6, 7, or 8 comprising producing a calix[n]pyrrole radical where n is 4, 5, 6, 7, or 8; and reacting the radical with a radical acceptor molecule.

33. A method of making a calix[n]pyrrole wherein n is 5, 6, 7, or 8 comprising reacting a pyrrole and a ketone in the presence of a Lewis acid.

34. The method of claim 33 wherein the Lewis acid is a high-valent metal-containing compound or boron trifluoride.

35. The method of claim 33 wherein n is 5.

36. The method of claim 33 wherein n is 6.

37. A method of making a calix[n]pyrrole wherein n is 4, 5, 6, 7, or 8 comprising reacting a pyrrole and a ketone in the presence of a heterogenous catalyst.

38. The method of claim 37 wherein the heterogenous catalyst is montmorillonite, zeolite, silica gel, alumina, or a cation exchange solid support.

39. The method of claim 37 wherein n is 5.

40. A method of making a calix[n]pyrrole wherein n is 4, 5, 6, 7, or 8 comprising reacting a pyrrole and a ketone in the presence of an anion template.

41. A method of making a calix[n]pyrrole wherein n is 4, 5, 6, 7, or 8 comprising
a) reacting a ketone-functionalized pyrrole and an alkyl or aryl metal to form a pyrrole alcohol,
b) condensing the pyrrole alcohol to form a cyclizable pyrrole oligomer; and
c) repeating step b) at least n-2 times to form a calix[n]pyrrole.

42. The method of claim 41 wherein the alkyl metal is a Grignard reagent or alkyl lithium.

43. The method of claim 41 wherein n is 5.

44. A method of making a solid-supported calix[n]pyrrole comprising

attaching a calix[n]pyrrole having a functionalized group to a solid support, the solid support reactive with the functionalized group, or to a tether-functionalized solid support, the tether reactive with the functionalized group.

45. A method of making a solid-supported calix[m]pyridino[n]pyrrole comprising

attaching a calix[m]pyridino[n]pyrrole having a functionalized group to a solid support, the solid support reactive with the functionalized group; or to a tether-functionalized solid support, the tether reactive with the functionalized group.

46. A method of making a solid-supported calix[m]pyridine comprising

attaching a calix[m]pyridine having a functionalized group to a solid support, the solid support reactive with the functionalized group, or to a tether-functionalized solid support, the tether reactive with the functionalized group.

47. A calix[n]pyrrole made by the method of claim 21, 23, 25, 26, 27, 30, 32, 33, 37, 40, 41, or 42.

48. A method of forming a complex of a calix[n]pyrrole or a calix[m]pyridino[n]pyrrole and an anion or a neutral molecule, comprising contacting the calix[n]pyrrole or the calix[m]pyridino[n]pyrrole with the anion or neutral molecule under conditions effective to allow the formation of the complex.

49. A method for separating a first molecule, a first anion, or first cation from a mixture of molecules, anions or cations, comprising

obtaining a calix[n]pyrrole-, a calix[m]pyridino[n]pyrrole- or a calix[m]pyridine-derivatized solid support; and

contacting the solid support with the mixture of molecules, anions or cations to separate the first molecule, the first anion or the first cation.

50. The method of claim 49 wherein the solid support is in the form of a chromatography column.

51. The method of claim 49 wherein the solid support is in the form of a capillary electrophoresis tube.

52. The method of claim 49 wherein the contacting is in a batch process.

53. The method of claim 49 wherein the solid support is a calix[n]pyrrole- or a calix[m]pyridino[n]pyrrole-solid support, the method is for separating a first anion, and the first anion is fluoride, phosphate, a phosphorylated molecule, or nitrate.

54. The method of claim 49 wherein the solid support is a calix[n]pyrrole- or a calix[m]pyridino[n]pyrrole-solid support, the method is for separating a first molecule, and the first molecule is a nucleotide or an oligonucleotide.

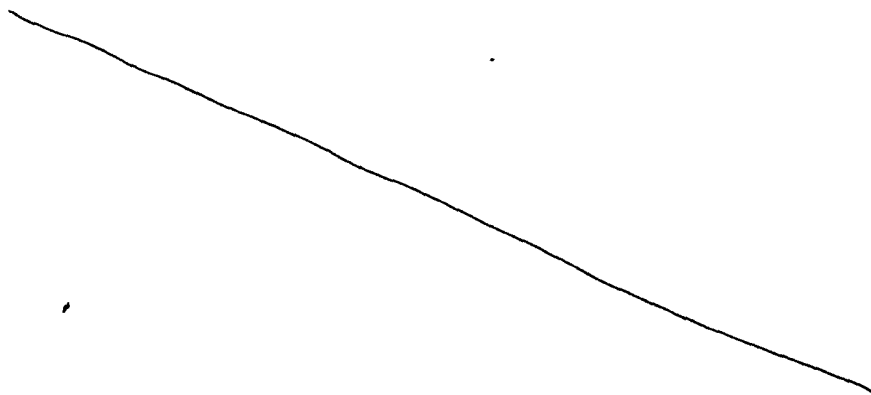
55. The method of claim 49 wherein the method is for separating a first anion or a first cation, and

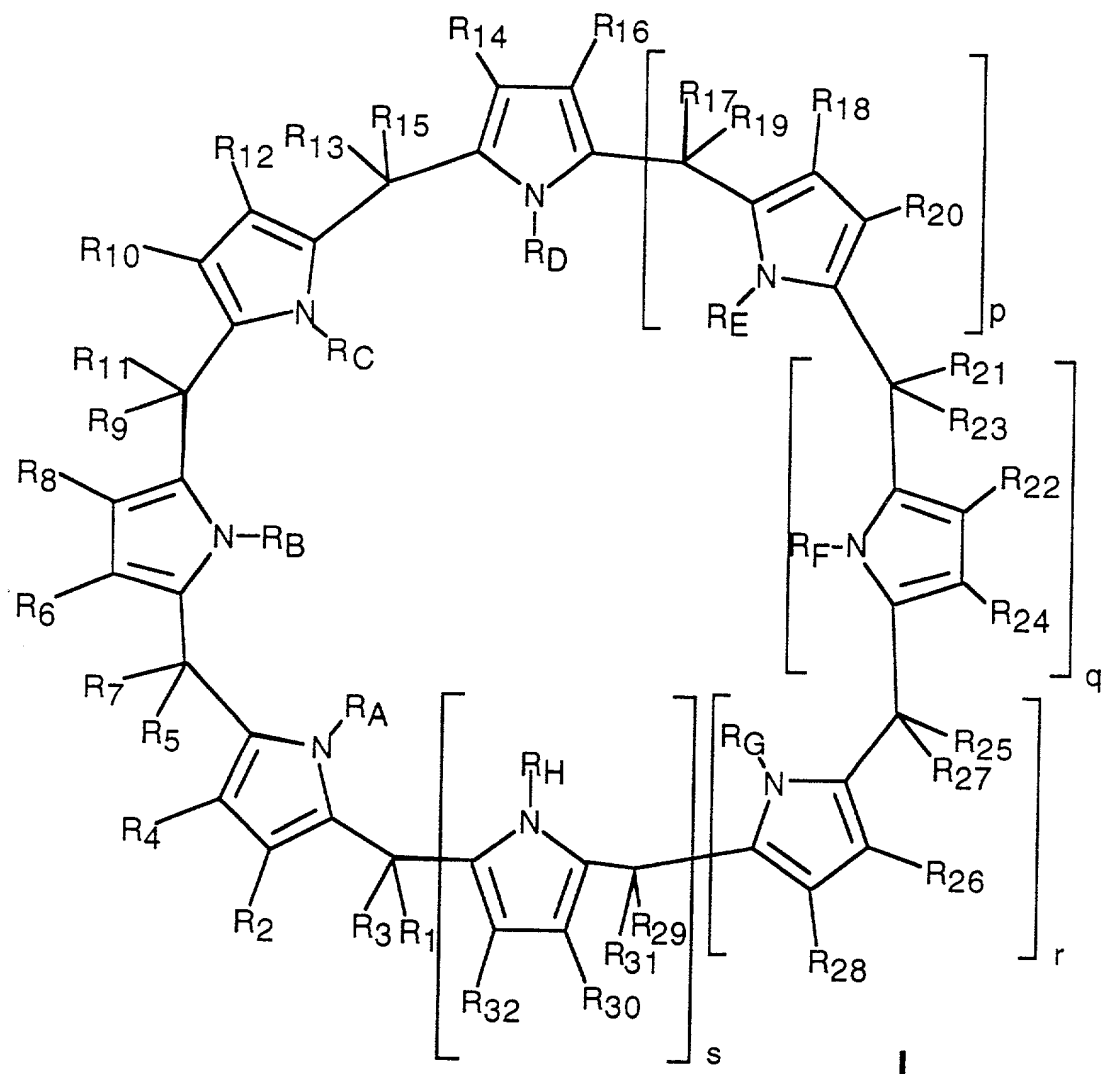
the first anion is an atomic anion or an molecular anion, or

the first cation is a atomic cation or a molecular cation.

56. The method of claim 49 wherein the method is for separating a first molecule, and the first molecule is a neutral, cationic or anionic aromatic molecule.

57. The method of claim 49 wherein the solid support is a calix[n]pyrrole solid support and the calix[n]pyrrole has structure I:





wherein

n is 4, 5, 6, 7 or 8;

when n is 4, $p = q = r = s = 0$, $R_1 - R_{16}$ are independently substituents as listed in paragraph i) below, and $R_A - R_D$ are independently substituents as listed in paragraph ii) below;

when n is 5, $p = 1$, $q = r = s = 0$, R_1 to R_{20} are independently substituents as listed in paragraph i) below, and $R_A - R_E$ are independently substituents as listed in paragraph ii) below;

when n is 6, $p = q = 1$, $r = s = 0$, R_1 to R_{24} are independently substituents as listed in paragraph i) below, and $R_A - R_F$ are independently substituents as listed in paragraph ii) below;

when n is 7, $p = q = r = 1$, $s = 0$, R_1 to R_{28} are independently substituents as listed in paragraph i) below, and $R_A - R_G$ are independently substituents as listed in paragraph ii) below;

when n is 8, $p = q = r = s = 1$, R_1 to R_{32} are independently substituents as listed in paragraph i) below, and $R_A - R_H$ are independently substituents as listed in paragraph ii) below;

i) hydrogen, halide, hydroxyl, alkyl, alkenyl, alkynyl, aryl, alkylaryl, nitro, phospho, formyl, acyl, hydroxyalkyl, alkoxy, hydroxyalkoxy, hydroxyalkenyl, hydroxyalkynyl, saccharide, carboxy, carboxyalkyl, carboxyamide, carboxyamidealkyl, amino, amido, aminoalkyl, phosphoalkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, tetrahydropyran, tetrahydrothiapyran, thioalkyl, haloalkyl, haloalkenyl, haloalkynyl, alkyl ester, a site-directing molecule, a catalytic group, a reporter group, a binding agent, or a couple that is coupled to a site-directing molecule, to a catalytic group, to a reporter group, or to a binding agent;

ii) a lone pair of electrons, hydrogen, alkyl, aminoalkyl, alkylsulfone, carboxy alkyl, carboxyamidealkyl, phospho alkyl, alkyl sulfoxide, alkyl sulfone, alkyl sulfide, halo alkyl, aryl, N-oxide, dialkylamino, carbamate, or arylsulfonyl;

or

at least two substituents are coupled to form a bridged structure, and when coupled to form a bridged structure, nonbridged substituents are as defined herein in paragraph i) or ii);

wherein

at least one R substituent is attached to the solid support;

at least one pyrrole nitrogen is bonded to hydrogen; and

odd-numbered R-substituents are other than hydrogen.

58. The method of claim 49 wherein the method is for separating a first anion, the solid support is a calix[n]pyrrole- or a calix[m]pyridino[n]pyrrole-solid support and the first anion is pertechnetate.

59. The method of claim 49 wherein the method is for separating a first molecule, the solid support is a calix[n]pyrrole- or a calix[m]pyridino[n]pyrrole-solid support and the first molecule is a polyhalobiphenyl.

60. The method of claim 59 where the polyhalobiphenyl is a polychlorobiphenyl.

61. The method of claim 49 wherein the method is for separating a first anion, the solid support is a calix[n]pyrrole- or a calix[m]pyridino[n]pyrrole-solid support, and the first anion is a phosphate anion.

62. A method of transporting a molecular or ionic species through a membrane comprising incorporating a calix[n]pyrrole or a calix[m]pyridino[n]pyrrole into the membrane; and contacting the membrane with the molecular or ionic species in the presence of a gradient of the molecular or ionic species or a counter gradient of a further species.

63. The method of claim 62 wherein the transporting results in the purification of the molecular or ionic species.

64. A method of binding a cation comprising contacting the cation with a calix[n]pyrrole or calix[m]pyridino[n]pyrrole having a cation-binding functionality, or with a calix[m]pyridine.

65. A method of removal of pertechnetate from pertechnetate-containing nuclear waste comprising contacting the waste with a calix[n]pyrrole or a calix[m]pyridino[n]pyrrole to form a calix[n]pyrrole or a calix[m]pyridino[n]pyrrole pertechnetate complex; and removing the complex from the waste.

66. A method of removal of an environmental pollutant from an environmental source, comprising contacting the environmental source with a calix[n]pyrrole or a calix[m]pyridino[n]pyrrole to form a calix[n]pyrrole- or a calix[m]pyridino[n]pyrrole-pollutant complex, and removing the complex from the environmental source.

67. A chromatography column comprising a solid support bound to a calix[n]pyrrole where n is 4-8; to a calix[m]pyridino[n]pyrrole where m+n=4-8 and m is not 1 or 2; or to a calix[m]pyridine where m is 4-8.

68. A sensor comprising a solid support bound to a calix[n]pyrrole where n is 4-8; to a calix[m]pyridino[n]pyrrole where m+n=4-8 and m is not 1 or 2; or to a calix[m]pyridine where m is 4-8.

69. Use of a calix[n]pyrrole, a calix[m]pyridino[n]pyrrole, or a calix[m]pyridine in the preparation of a pharmaceutical composition for use in *in vivo* or *ex vivo* treatment of body tissues.

70. The use of claim 69 wherein the treatment is *ex vivo* and is kidney dialysis.

71. The use of claim 69 wherein the treatment is removal of urea for treatment of gout.

72. An electropolymerizable calix[n]pyrrole, calix[m]pyridino[n]pyrrole, or calix[m]pyridine.

73. An anion-, cation-, or neutral molecule-selective electrode comprising
a conductive body,
a polymer, and
a calix[n]pyrrole, a calix[m]pyridino[n]pyrrole, or a calix[m]pyridine.

74. The electrode of claim 73 wherein the calix[n]pyrrole, the calix[m]pyridino[n]pyrrole, or the calix[m]pyridine is electropolymerized and forms the conductive body.

75. A method of electrochemical detection of an anion, a cation, or a neutral molecule comprising
assembling the anion-, cation-, or neutral molecule-selective electrode of claim 73;
contacting the electrode with a solution of the anion, the cation, or the neutral molecule;
and
determining the presence or absence of the anion, the cation, or the neutral molecule.

76. The method of claim 66 wherein the pollutant is a polyhalobiphenyl compound, a nitrate compound, or a phosphate compound.

77. A method of making a calixpyridinopyrrole comprising:
adding halocarbene to calixpyrrole in a cycloaddition reaction,
thereby converting a pyrrole to a pyridine and forming a calixpyridinopyrrole.

78. A method of making a calixpyridine comprising:
adding halocarbene to calixpyrrole or to calixpyridinopyrrole in a cycloaddition reaction
so as to convert pyrrole to pyridine to form a calixpyridine.

79. The macrocycle of claim 1 wherein the ionic species is an anionic species.

80. A *meso*-substituted calix[n]pyrrole macrocycle where n is 4, 5, 6, 7, or 8 wherein the
meso-substitution is an oxygen-, sulfur-, or alkenyl-containing substituent; or is a couple to a
site-directing molecule, to a binding agent, or to a reporter group.

81. A β -substituted calix[n]pyrrole, calix[m]pyridino[n]pyrrole or calix[m]pyridine.

82. The macrocycle of claim 80 wherein the *meso*-substitution is a couple to a site-directing
molecule and the site-directing molecule is an oligonucleotide, an antibody, or a peptide having
affinity for a biological receptor.

83. The macrocycle of claim 80 wherein the *meso*-substitution is a couple to a binding agent
and the binding agent is a calix[n]pyrrole, a calix[m]pyridino[n]pyrrole, a calixarene, a cation-
binding functionality, a crown ether, a chelating group, a porphyrin, or an expanded porphyrin.

84. The macrocycle of claim 80 wherein the *meso*-substitution is a couple to a reporter group
and the reporter group is a redox active group, or a fluorescent molecule.

85. The macrocycle of claim 84 wherein the reporter group is a redox active group and the
redox active group is ferrocene.

86. The macrocycle of claim 80 wherein the *meso*-substitution is an oxygen-containing
substituent and the oxygen-containing substituent is carboxy or carboxyalkyl.

87. The macrocycle of claim 80 wherein at least one β -carbon has a substituent other than hydrogen.

88. The macrocycle of claim 80 wherein at least one β -carbon has a carboxy, carboxyalkyl, ester, or carboxyamide substituent.

89. The macrocycle of claim 80 wherein at least one macrocyclic nitrogen is bound to hydrogen.

90. A macrocycle selected from the group consisting of compounds 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, and 42.

91. A calix[m]pyridino[n]pyrrole macrocycle where $m + n$ is 4, 5, 6, 7, or 8 and m and n are other than 1 and 3 or 2 and 2, respectively; or a calix[m]pyridine macrocycle where m is 4, 5, 6, 7, or 8; the macrocycle noncovalently complexed to a molecular or cationic species.

92. A method of making a calix[n]pyrrole where n is 4, 5, 6, 7, or 8 comprising reacting a pyrrole and an n -fold cyclic ketone template to form the calix[n]pyrrole.

93. The method of claim 92 wherein the cyclic ketone template is a calix[n]arene.

94. The method of claim 92 wherein the pyrrole is a β -substituted pyrrole.